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(54) **Translucent thermoplastic elastomers.**

(57) Thermoplastic elastomers having the property of optical translucence are provided by incorporating syndiotactic polypropylene homopolymer into olefinic elastomers. The rubber component of the composition is at least partially cured.

EP 0 670 350 A1

BACKGROUND OF THE INVENTION**Field of the Invention**

5 This invention relates to thermoplastic elastomers which are optically translucent. A thermoplastic elastomer is generally defined as a polymer or blend of polymers that can be processed and recycled in the same way as a conventional thermoplastic material, yet has properties and performance similar to that of vulcanized rubber at service temperatures. Blends or alloys of plastic and elastomeric rubber have become increasingly important in the production of high performance thermoplastic elastomers, particularly
 10 for the replacement of thermoset rubber in various applications.

Description of the Related Art

Polymer blends which have a combination of both thermoplastic and elastic properties are generally
 15 obtained by combining a thermoplastic polyolefin with an elastomeric composition in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous phase of the thermoplastic. Early work with vulcanized compositions is found in U.S. Pat. No. 3,037,954 which discloses static vulcanization as well as the technique of dynamic vulcanization wherein a vulcanizable
 20 elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured while continuously mixing and shearing the polymer blend. The resulting composition is a micro-gel dispersion of cured elastomer, such as butyl rubber, chlorinated butyl rubber, polybutadiene or polyisobutene in an uncured matrix of thermoplastic polymer such as polypropylene.

In U.S. Pat. No. Re. 32,028 polymer blends comprising an olefin thermoplastic resin and an olefin copolymer rubber are described, wherein the rubber is dynamically vulcanized to a state of partial cure. The
 25 resulting compositions are reprocessable. U.S. Pat. Nos. 4,130,534 and 4,130,535 further disclose thermoplastic elastomer compositions comprising butyl rubber and polyolefin resin, and olefin rubber and polyolefin resin, respectively. The compositions are prepared by dynamic vulcanization and the rubber component is cured to the extent that it is essentially insoluble in conventional solvents. These products are usually opaque even if the individual components have high clarity or the compositions are unfilled. Such
 30 opaqueness is attributed to the presence of a two phase system whose domains are larger than the wavelength of light, as well as the color inherent in the compositions.

Flexible thermoset elastomers of good optical clarity have been prepared from EPDM rubber blended with very fine fumed silica and a silane coupling agent (U.S. Pat. No. 4,603,158). More recently polysiloxanes with substituent groups such as methyloctyl have been blended with styrene-ethylene-butylene
 35 styrene (SEBS) block copolymer to yield thermoplastic elastomers with good optical properties (U.S. Pat. No. 4,613,640). Also, polypropylene impact blends containing ethylene-propylene copolymers and low density polyethylene and having good optical properties have been described in U.S. Pat. Nos. 4,087,485 and 4,113,806. Unlike thermoplastic elastomers, such impact polymers have poor resistance to compression
 40 set.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that a thermoplastic elastomer composition having the property of optical translucence is provided by incorporating syndiotactic polypropylene homopolymer into
 45 olefinic thermoplastic elastomers, in combination with the olefin rubber component. The rubber component of the composition is usually present as micron-size particles in the thermoplastic matrix, and it is preferably at least partially cured. Unexpectedly, the inclusion of syndiotactic polypropylene homopolymer in the composition provides a thermoplastic elastomer which has a significantly lowered Gardner haze value, while maintaining the desirable properties of low compression set and thermal stability. The
 50 compositions have utility as molded mechanical rubber goods such as face masks and seals, as well as extruded articles such as flexible tubing and fluid delivery bags for medical and other applications.

DESCRIPTION OF THE PREFERRED EMBODIMENTS**POLYPROPYLENE**

The polypropylene used in the compositions of the invention is a crystalline material which is syndiotactic in structure. The stereochemistry of syndiotactic polypropylene is generally described as one

in which the polymer principally contains units of exactly alternating configuration, as opposed to the repeating units with identical configuration in isotactic polypropylene or the random configuration of atactic polypropylene. Syndiotactic polypropylene homopolymer has a density in the range of 0.89-0.91 g/cm³ and a melting point in the range of 135 - 140° C. It may be prepared by several known processes, including the use of ionic catalysts such as the reaction product of metallocene and an activator compound as described in published European Patent Application 548274. The syndiotactic polypropylene may contain minor amounts of isotactic or random polypropylene.

The amount of polypropylene found to provide useful translucent compositions is generally from about 10 to about 90 weight percent, based on the weight of the rubber and polypropylene. Preferably, the polypropylene content of the composition will range from about 25 to about 90 percent by weight, with a most preferred range of about 60 to about 90 percent by weight.

OLEFINIC RUBBER

Suitable olefin copolymer rubbers comprise non-polar, essentially non-crystalline, rubbery copolymers of two or more α -olefins, preferably copolymerized with at least one polyene, usually a diene. Saturated olefin copolymer rubber, for example ethylene-propylene copolymer rubber (EPM) can be used. However, unsaturated olefin rubber such as EPDM rubber is more suitable. EPDM is a terpolymer of ethylene, propylene and a non-conjugated diene. Satisfactory non-conjugated dienes include 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and the like. Blends of any of the above olefinic rubbers can be employed, rather than a single olefinic rubber.

In preparing the compositions of the invention, the amount of olefinic rubber generally ranges from about 90 to about 10 weight percent, based on the weight of the rubber and polypropylene. Preferably, the olefinic rubber content will be in the range of from about 74 to about 10 weight percent, with a most preferred range of about 40 to about 10 weight percent.

It is also preferred that the ethylene (C₂) content of the olefinic rubber be about 45 weight percent or higher. When the C₂ content of the rubber component is lower, the desired translucent properties of the compositions are greatly reduced. With C₂ content above about 45 weight percent, there appears to be a synergism between the syndiotactic polypropylene and the olefinic rubber which results in a significant improvement in translucence of the thermoplastic elastomer product. Olefinic rubbers having a C₂ content greater than about 65 weight percent are most preferred.

CURING AGENT

Those ordinarily skilled in the art will appreciate the appropriate quantities, types of cure systems and vulcanization conditions required to carry out the vulcanization of the rubber. The rubber can be vulcanized using varying amounts of curative, varying temperatures and varying time of cure in order to obtain the optimum crosslinking desired. Any known cure system for the rubber can be used, so long as it is suitable under the vulcanization conditions with the specific olefinic rubber or combination of rubbers being used and with the polyolefin. These curatives include sulfur, sulfur donors, metal oxides, resin systems, peroxide-based systems and the like, both with and without accelerators and co-agents. Peroxide curatives are preferred for the preparation of the translucent compositions of the invention, since they do not introduce color. Such cure systems are well known in the art and literature of vulcanization of elastomers.

PROCESSING

The olefin rubber component of the thermoplastic elastomer is generally present as micron or submicron size particles within a continuous polyolefin matrix. Alternatively, depending on mixing conditions and compositions, cocontinuous phase morphologies or a mixture of discrete and cocontinuous phase morphologies are also possible. The rubber is desirably at least partially crosslinked, and preferably is completely or fully crosslinked. The partial or complete crosslinking can be achieved by adding an appropriate rubber curative to the blend of polyolefin and rubber and vulcanizing the rubber to the desired degree under conventional vulcanizing conditions. However, it is preferred that the rubber be crosslinked by the process of dynamic vulcanization. As used in the specification and claims, the term "dynamic vulcanization" means a vulcanization or curing process for a rubber contained in a thermoplastic elastomer composition, wherein the rubber is vulcanized under conditions of high shear at a temperature above the melting point of the polyolefin component. The rubber is thus simultaneously crosslinked and dispersed as

fine particles within the polyolefin matrix, although as noted above other morphologies may also exist. Dynamic vulcanization is effected by mixing the thermoplastic elastomer components at elevated temperature in conventional mixing equipment such as roll mills, Banbury mixers, Brabender mixers, continuous mixers, mixing extruders and the like. The unique characteristic of dynamically cured compositions is that, notwithstanding the fact that the rubber component is partially or fully cured, the compositions can be processed and reprocessed by conventional plastic processing techniques such as extrusion, injection molding and compression molding. Scrap or flashing can be salvaged and reprocessed.

The terms "fully vulcanized" and "completely vulcanized" as used in the specification and claims means that the rubber component to be vulcanized has been cured to a state in which the elastomeric properties of the crosslinked rubber are similar to those of the rubber in its conventional vulcanized state, apart from the thermoplastic elastomer composition. The degree of cure can be described in terms of gel content or, conversely, extractable components. Alternatively the degree of cure may be expressed in terms of crosslink density. All of these descriptions are well known in the art, for example in U.S. Pat. Nos. 5,100,947 and 5,157,081, both of which are fully incorporated herein by this reference.

The following general procedure was used in the preparation of thermoplastic elastomers of the invention, as set forth in the examples. The rubber plus peroxide curative and a coagent were mixed in a Brabender mixer of 80 cc capacity at 100 rpm. The temperature in the mixer was maintained below about 130 °C in order to disperse the curative without prematurely vulcanizing the rubber. The mix was then combined with the polypropylene and masticated under nitrogen at a temperature in the range of 160-190 °C to dynamically vulcanize the rubber in the blend. When the cure was as complete as desired an antioxidant was added and mixing continued for up to about 15 minutes.

Nucleating agents for polypropylene, such as Millad 3905, may also be added in small amounts (0.1 to 1.0 phr) but mixing must then be carried out at 230 °C.

Compression molded plaques of about 1.6 mm thickness were prepared at about 200 °C from the dynamically vulcanized alloy (DVA), followed by cooling in the mold to minimize distortion. These test plaques were used for the measurement of physical and optical properties. Haze of the compositions was measured following the procedure of ASTM D 1003-61, with a Gardner brand Model XL-211 hazemeter. In this measurement a completely opaque material has a reading of 100%, and lower values indicate better optical clarity. No attempt was made to prepare plaques having "smooth" surfaces, and therefore the measured haze values are higher than if the plaques had an optically smooth texture.

The present invention will be better understood by reference to the following examples which serve to illustrate but not limit the invention.

Example 1

Dynamic vulcanizates were prepared following the general procedure described above, with syndiotactic polypropylene, isotactic polypropylene, random tacticity polypropylene and impact modified polypropylene. The elastomer component of the composition was selected from EPDM rubbers having ethylene (C₂) content in the range of 48-77%. The ratio of components was 76 weight percent EPDM rubber and 24 weight percent polypropylene. The compositions also included 0.51 phr (parts per hundred rubber) of α - α' -bis (t-butyl peroxy)diisopropylbenzene curative, 1.65 phr of tri-allyl cyanurate coagent and 1.5 phr of bis-(2,4-di-t-butylphenyl) pentaerythritol diphosphate antioxidant. Plaques were prepared from the finished compositions as described above, and haze values were determined. Results are set forth in Table I.

TABLE I

	% Haze		
	EPDM "A" (48% C ₂)	EPDM "F" (74% C ₂)	EPDM "G" (77% C ₂)
Impact polypropylene	--	100%	--
Isotactic polypropylene	100	100	100
Random polypropylene	100	71	78
Syndiotactic polypropylene "1"	86	39	36
Syndiotactic polypropylene "2"	--	36	--
Syndiotactic polypropylene "3"	--	27	--

As demonstrated by these results, thermoplastic elastomers prepared using syndiotactic polypropylene homopolymer show a striking improvement in optical translucence, as compared with compositions containing isotactic, random or impact forms of polypropylene.

5 Example 2

Dynamic vulcanizates were prepared using the general method described above, with syndiotactic polypropylene "1" homopolymer and EPDM rubbers having C₂ contents in the range of 48-77 percent. In all cases the ratio of EPDM to polypropylene was 75/25, and the curatives and antioxidant were as set forth
10 in Example 1. The compositions were prepared using total mixing times of seven minutes and fifteen minutes respectively. Plaques were prepared and haze values determined as described above. The results are set forth in Table II.

TABLE II

EPDM	Wt. % C ₂	Haze Values (%)	
		7 min. mixing	15 min. mixing
"A"	48	90	86
"B"	68	70	53
"C"	70	65	60
"D"	71	58	51
"E"	72	69	57
"F"	74	48	29
"G"	77	46	36

It can be seen from these results that the ethylene content of the rubber component has a synergistic effect on the optical characteristics of the thermoplastic elastomers. Higher C₂ content provides a product of increased clarity, while a C₂ content below about 48 weight percent provides little if any of the translucent
30 properties desired in the compositions of the invention. A longer mixing period after vulcanization of the blend also improves the optical properties in most instances, probably due to a reduction in particle size of the cured elastomer thus reducing the tendency to scatter light.

35 Example 3

A series of dynamic vulcanizates was prepared over a range of EPDM/polypropylene ratios, using the method described above. The curatives and antioxidant were as in Example 1, and mixing time was 12-15 minutes. Plaques were prepared and haze values determined. The results are shown in Table III.

TABLE III

	EPDM/PP (76/24)	EPDM/PP (50/50)	EPDM/PP (29/71)
EPDM "F", phr	100	100	100
Polypropylene "1", phr	32	100	250
Gardner haze, %	40	54	66

The translucent compositions of the invention can be prepared over a broad range of rubber/polypropylene ratios.

Example 4

Compositions of the invention were prepared including a mineral oil additive to determine the effect of
55 oil on optical clarity. Thermoplastic elastomers were prepared as described above, using a rubber/polypropylene ratio of 75/25 and a total mixing time of about 25 minutes. Plaques were prepared and both optical and physical properties were determined. Results are set forth in Table IV.

TABLE IV

	I	II	III	IV
EPDM "F", phr	100	100	--	--
EPDM "G", phr	--	--	100	100
Polypropylene "1", phr	32	32	32	32
Mineral oil ¹ , phr	0	48	0	48
Curative ² , phr	0.51	0.51	0.51	0.51
Coagent ² , phr	1.65	1.65	1.65	1.65
Antioxidant ² , phr	1.5	1.5	1.5	1.5
Hardness (Shore A)	88	65	85	58
Stress at 100% strain ³ (MPa)	4.7	7.1	5.6	7.0
Tensile strength ³ (MPa)	10.3	9.6	7.8	9.8
Elongation at break ³ (%)	374	402	187	391
Compression set ⁴ (%) (22 hours/100 °C)	39	27	33	--
Haze (%)	40	38	33	40

¹ fully saturated paraffinic oil [HT Brightstock, from Petrocanada]

² same as in Example 1

³ ASTM D 412

⁴ ASTM D 395B

As can be seen from these results, the inclusion of mineral oil had no significant effect on the optical properties of the DVAs.

The components used in the foregoing examples are described in Table V.

TABLE V

Polypropylene "1"	Syndiotactic homopolymer [Grade G49M, Hoechst AG]
Polypropylene "2"	Syndiotactic homopolymer [Grade G53, Hoechst AG]
Polypropylene "3"	Syndiotactic homopolymer [Grade G20/28, Hoechst AG]
Random polypropylene	Random tacticity copolymer [Escorene PD9272, Exxon]
Isotactic polypropylene	Isotactic homopolymer [Rexene 11s07a, Lyondel]
Impact polypropylene	Impact modified copolymer [Escorene 7031, Exxon]
EPDM "A"	Ethylene-propylene-diene terpolymer [Vistalon 4608, Exxon]
EPDM "B"	Ethylene-propylene-diene terpolymer [Vistalon 707, Exxon]
EPDM "C"	Ethylene-propylene-diene terpolymer [Vistalon 7000, Exxon]
EPDM "D"	Ethylene-propylene-diene terpolymer [Epsyn 5508, Copolymer]
EPDM "E"	Ethylene-propylene-diene terpolymer [Dutral 033/E, Montedison]
EPDM "F"	Ethylene-propylene-diene terpolymer [Vistalon 8731, Exxon]
EPDM "G"	Ethylene-propylene-diene terpolymer [Nordel 2722, Dupont]

While the best mode and preferred embodiment of the invention have been set forth in accord with the Patent Statutes, the scope of the invention is not limited thereto, but rather is defined by the claims which follow.

Claims

1. An optically translucent composition comprising
 - a) thermoplastic syndiotactic polypropylene homopolymer, and
 - b) elastomeric ethylene- α -olefin polymer
 wherein said elastomeric polymer is at least partially cured.
2. The composition of claim 1 wherein the elastomeric polymer is an ethylene-propylene copolymer.

3. The composition of claim 1 wherein the elastomeric polymer is an ethylene-propylene-nonconjugated diene terpolymer.
4. The composition of claim 1 wherein the elastomeric polymer has an ethylene content of at least about 45 wt %.
5. The composition of claim 1 wherein the elastomeric polymer has been cured with a peroxide curing agent.
6. The composition of claim 1 comprising from about 10 to about 90 parts of polypropylene and from about 90 to about 10 parts elastomeric polymer per 100 parts of polypropylene and elastomeric polymer.
7. The composition of claim 1 wherein the elastomeric polymer is fully cured by dynamic vulcanization.
8. The composition of claim 1 in the form of a molded or extruded optically translucent article.
9. The composition of claim 1 prepared by the steps of
 - a) mixing elastomeric ethylene- α -olefin polymer and a curative until the curative is evenly dispersed in the mixture,
 - b) blending the mixture from step (a) with syndiotactic polypropylene, and
 - c) masticating the blend from step (b) under shear at a temperature in the range of about 160 °C to about 190 °C until the elastomeric polymer is at least partially cured.
10. An optically translucent composition comprising
 - a) from about 25 to about 90 wt % of thermoplastic syndiotactic polypropylene homopolymer, and
 - b) from about 10 to about 75 wt % elastomeric EPDM terpolymer rubber having an ethylene content greater than about 65 wt %, wherein said rubber is at least partially cured by dynamic vulcanization in the presence of a peroxide curing agent.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 2938

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP-A-0 618 259 (MITSUI TOATSU CHEMICALS, INC.) * claims; examples 1-3,5 *	1-10	C08L23/12 C08L23/16
D,Y	US-A-4 087 485 (TERRENCE HUFF) * column 3, line 38 - line 37; claims; example 1 *	1-10	
Y	EP-A-0 499 216 (MITSUI TOATSU CHEMICALS, INC.) * page 2, line 25 - line 33; claims *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 June 1995	Examiner Clemente Garcia, R.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	